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Ugi amine-derived *P,N*- and *P,P*-ligands with *N*-alkyltriethoxysilyl tethers: synthesis and evaluation of mesoporous silica-supported Pd complexes in asymmetric allylic substitution reactions

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ABSTRACT

A facile approach to the synthesis of several types of chiral *P,N*- and *P,P*-ligands bearing triethoxysilyl groups starting from *N,N*-diemthyl-1-ferrocenylethylamine (Ugi amine) has been developed. Allyl palladium complexes of these ligands have been prepared, characterized, and grafted on mesoporous silica. The resulting silica-supported complexes have been shown to catalyze asymmetric allylic alkylation and aminations reactions with moderate enantioselectivities.

1. Introduction

Last decade has seen a tremendous increase in the number of publications on heterogeneous catalysts comprised of well-organized organometallic homogeneous catalysts supported on polymer matrices or inorganic materials, such as a mesoporous silica, and aimed at easy separation from a reaction mixture and recoverability in specialty chemicals synthesis.[1] A significant progress has been achieved in the development of supported catalysts for asymmetric allylic substitution reactions comparable in their activity and stereoselectivity to their homogeneous counterparts.[2] While most of the success has been associated with the use of polymeric matrices, progress toward the development of viable silica-supported catalysts is lagging far behind.[3] In part, this could be attributed to difficulties associated with the synthesis and purification of ligands containing trialkoxysilyl groups (usually-ethyl) necessary for their anchoring on a silica surface. A decade ago Thomas and co-workers[4a] have reported on the synthesis and catalytic properties of MCM-41 silica-supported palladium dichloride complex **12** with Ugi amine[5] (**1**)-derived *P,P*-ligand (Fig. 1). Complex **12** capable of catalyzing the allylic amination of cinnamyl acetate with benzyl amine yielding 50% of the branched product with 93–99% ee was prepared via a nucleophilic substitution reaction between the corresponding *N,N′*-dimethylethylenediamine derivative of Ugi amine and propylbromide chains supported on the inner walls of the silica. Thus, a synthetic procedure involving ferrocenyl intermediates bearing triethoxysilyl groups was avoided. In other cases relevant to the incorporation of triethoxysilyl groups into a ligand based on the Ugi amine structure this has been achieved through the formation of amide bonds between either a carboxylic group of a ligand precursor and an amino-group of a bifunctional linker molecule bearing a triethoxysilyl[3] or an amino-group of the former and isocyano-group of the latter.[6] The obvious limitation of the above methods is mandatory introduction of additional heteroatoms into the ligand structure barring the simple alkyl and oxa-alkyl motifs from consideration as a tether. Although Thomas and co-workers[4b] have prepared a ligand featuring a simple propyl linker by reacting 1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethyl acetate, **3a** (Fig. 1) with 3-(methylamino)-1-(trimethoxysilyl)propane, this method can hardly be considered as general. Intrigued by a possible dependence of the catalytic properties of silica-supported Pd complexes with alkyl tethers on the length of a tether and the presence of oxygen atom(s) in them, the synthesis of a $(CH_2)_2O(CH_2)_3$-analog of Thomas' compound from **3a** was attempted. A large excess (12–14 equiv) of $MeNH(CH_2)_2O(CH_2)_3Si(OEt)_3$ prepared via a multistep synthesis (see Supplementary data) was required, with isolated yields never exceeding 15–20% in our hands. Moreover, recycling of the aminoalkylsilane was not an option as it has proven

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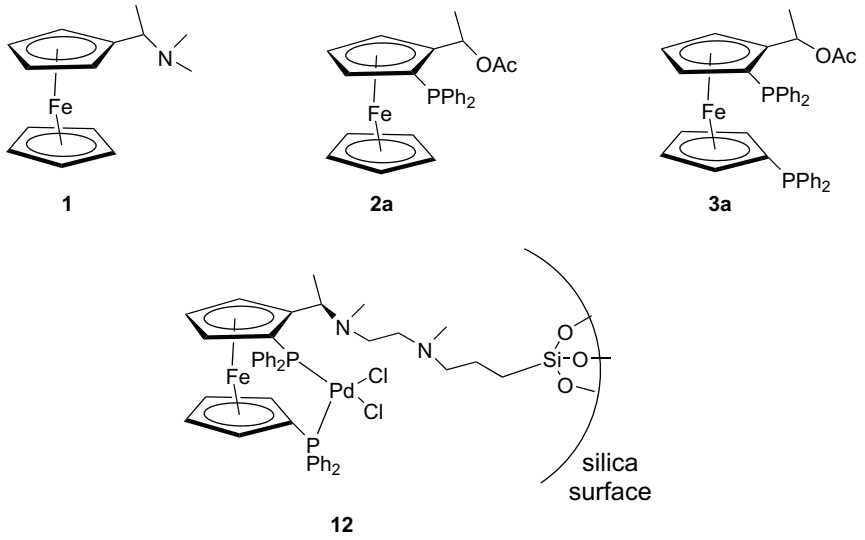


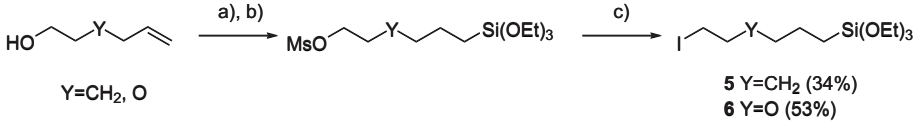
Fig. 1. Ugi amine **1** and structurally related acetates **2a**, **3a**, and complex **12**.

difficult to recover from the reaction mixtures. It became clear that the approach based on the reaction of an aminoalkylsilane with acetates **2a** and **3a** is limited only to the aminoalkylsilanes readily available in multigram quantities. Herein we would like to report on an alternative approach to the synthesis of such ligands as well as on the grafting of their allyl palladium complexes on a mesoporous silica and the performance of resulting asymmetric supported catalysts in allylic alkylation and amination reactions.

2. Results and discussion

2.1. Syntheses of ferrocenyl chiral ligands bearing triethoxysilylalkyl tethers

At the outset of this work introduction of triethoxysilyl group via a transition metal-catalyzed hydrosilylation of appropriate ligand precursors derived from **2b** and **3b**, both common intermediates used for the synthesis of various phosphinoferrocenyl ethylamine ligands, as late as possible in the overall synthesis seemed particularly attractive as this would allow to minimize the number of synthetic steps labile the triethoxysilyl group has to be carried over. However, this approach did not bear fruit as attempted hydrosilylations of *N*-methyl-*N*-(1″-(3″-oxa-5″-hexenyl))-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine and *N*-methyl-*N*-(1′-(3′-oxa-5′-hexenyl))-1-[2-(diphenylphosphinyl)ferrocenyl]ethylamine (a phosphine oxide) with triethoxysilane in the presence of Karstedt's catalyst both failed (see Supplementary data). Apparently, the ligating groups present in these molecules rendered the platinum catalyst inactive.[7] As a result, we turned our attention to N-alkylation of **2b** and **3b** with an appropriate reagent already bearing a triethoxysilyl group. Initially this approach did not seem to be very promising due to seemingly unavoidable formation of alkyl ammonium and phosphonium salts and their mixtures in addition to desired tertiary amines. Moreover, our early attempts with an alkyl tosylate as the alkylation reagent have failed. However, reports by Toma and coworkers[3] on the alkylations of **2b** and **3b** with methyl 5-bromovalerate in the presence of potassium carbonate in acetone furnishing the corresponding tertiary amines in almost 90% yield encouraged us to reconsider. In our experiments bromides were replaced with iodides in an attempt to decrease the reaction temperature. Acetonitrile was used instead of acetone due to its both ease of drying and superiority as a solvent in S_N2 reactions. Although it took about 4.5 days for a room temperature reaction between **2b** and 1-iodo-3-(triethoxysilyl)propane, **4**,[8] to go to completion, to our delight, it produced a relatively simple mixture, the expected tertiary amine being a major product. However, it was isolated in dismal 3% yield after column chromatography on silica gel. A distinct orange-brown color of the upper part of the column packing suggested that most of the product did not reach the end of the column due to the condensation reaction between its triethoxysilyl groups and hydroxyl groups on the surface of silica, which was, ironically, the very same reaction that our ligand had been intended to be engaged in at a later stage of this study. Repeated washing of the reaction product mixture with hexane, although useful for the separation from the ionic compounds, did not provide separation from the unreacted secondary amine. Fortunately, column chromatography on C18 reversed-phase silica gel with acetonitrile as an eluent allowed for the isolation of pure tertiary amines without their condensation with silica surface. Increasing the alkylation reaction temperature to 40 °C not only resulted in significant shortening of the reaction time to about 39 h, but also seemed to have slightly benefited the formation of the tertiary amine product. To check the applicability of the alkylation approach to different α,ω-iodo(trialkoxysilyl)alkanes, 1-iodo-6-(triethoxysilyl)hexane, **5**, and 1-iodo-6-(triethoxysilyl)-3-oxahexane, **6**, were prepared from the corresponding alcohols via a sulfonylation–hydrosilylation-nucleophilic substitution sequence (Scheme 1) previously used in our synthesis of 1-triethoxysilyl-6-azido-4-oxahexane.[9]



Scheme 1. (a) MsCl, CH_2Cl_2, 0 °C, (b) $HSi(OEt)_3$, Karstedt cat., THF 35 °C, (c) NaN_3, DMF, 60 °C.

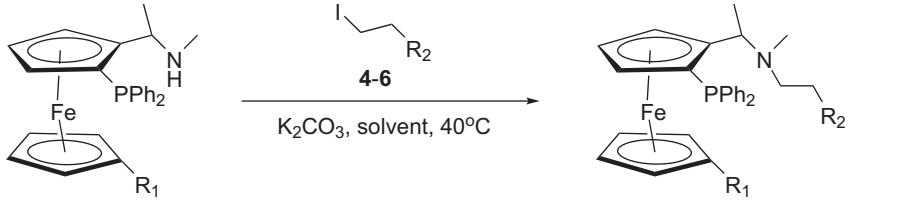
Alkylation with **6** containing oxygen in β-position was substantially slower (60 h) compared with both **4** and **5** for which there was no discernable difference in the reaction rates. The isolated yield of the tertiary amine in case of **6** was also the lowest among the three α,ω-iodo(trialkoxysilyl)alkanes (Table 1, entries 1–3). Although the separation method worked well in all three cases, the best separation of the tertiary amine band from that of unreacted **2b** was achieved for the least polar tertiary amine with 1-(triethoxysilyl)hexyl-substituent. Due to a higher retention time of this tertiary amine, it was also the most time-consuming. All three tertiary amines isolated as dark-orange viscous oils could be handled in air without oxidation. However, freshly prepared solutions of all three compounds in $CDCl_3$ have shown signs of oxidation in both their ^1H and $^{31}P\{^1H\}$ NMR spectra within less than 1 h.

substituents were also prepared using the acylation–amide reduction method (see Supplementary data).

2.2. Allyl palladium complexes: synthesis and grafting on mesoporous silica

From the outset of this work our goal has been the immobilization on silica of fully-characterized palladium complexes, not ligands, in order to avoid dealing with characterization and possible purification of the supported ligands prior to their complexation with palladium. Stirring a mixture of a ligand with $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2:1 M ratio) in dichloromethane followed by removal of the solvent provided crude complexes $[(\eta^3\text{-}C_3H_5)Pd(\mathbf{2c}–\mathbf{e})Cl]$ and $[(\eta^3\text{-}C_3H_5)Pd(\mathbf{3d})Cl]$. Although the ^1H NMR spectra (in $CDCl_3$) of semi-solids

Table 1
Synthesis of ligands via alkylation of **2b** and **3b** by alkyl iodides **4**–**6**



2b, R_1=H
3b, R_1=PPh_2

4a, R_2=$CH_2Si(OEt)_3$
b, R_2=CH_3
5a, R_2=$(CH_2)_4Si(OEt)_3$
b, R_2=$(CH_2)_4H$
6a, R_2=$O(CH_2)_3Si(OEt)_3$
b, R_2=$O(CH_2)_3H$

2c, R_1=H, R_2=$CH_2Si(OEt)_3$
2d, R_1=H, R_2=$(CH_2)_4Si(OEt)_3$
2e, R_1=H, R_2=$O(CH_2)_3Si(OEt)_3$
2f, R_1=H, R_2=CH_3
2g, R_1=H, R_2=$(CH_2)_4H$
2h, R_1=H, R_2=$O(CH_2)_3H$
3c, R_1=PPh_2, R_2=$CH_2Si(OEt)_3$
3d, R_1=PPh_2, R_2=$(CH_2)_4Si(OEt)_3$
3e, R_1=PPh_2, R_2=$O(CH_2)_3Si(OEt)_3$

Ligand	R_1	R_2	Reaction solvent	Reaction time, h	Isolated yield, %
2c	H	$CH_2Si(OEt)_3$	CH_3CN	39	57
2d	H	$(CH_2)_4Si(OEt)_3$	CH_3CN	39	65
2e	H	$O(CH_2)_3Si(OEt)_3$	CH_3CN	60	46
2f[a]	H	CH_3	CH_3CN	40	69
2g[a]	H	$(CH_2)_4H$	CH_3CN	40	65
2h[a]	H	$O(CH_2)_3H$	CH_3CN	60	42
3c	PPh_2	$CH_2Si(OEt)_3$	CH_3CN	41	33
3c	PPh_2	$CH_2Si(OEt)_3$	CH_3CN–CH_2Cl_2 (4:1)	40	45
3d	PPh_2	$(CH_2)_4Si(OEt)_3$	CH_3CN–CH_2Cl_2(2:1)	40.5	48
3e	PPh_2	$O(CH_2)_3Si(OEt)_3$	CH_3CN	90	24

[a] Provided for comparison.

Due to the presence of an additional nucleophilic site, it is not surprising that alkylation of **3b** furnished tertiary amines in lower yields compared to those of **2b**. Thus, in case of **6** both the yield and reaction time were at disadvantage compared to the monophosphine case (Table 1, entries 3 and 10). Addition of dichloromethane to acetonitrile was found to improve the yields of tertiary amines. As **3b** is less soluble in acetonitrile than its monophosphine counterpart, mixing 1 equiv of it with 1 equiv of an alkylation reagent in this solvent alone creates a large excess of the alkylation reagent leading to easy overalkylation. The addition of dichloromethane is likely to alleviate this problem somewhat by increasing the solubility of **3b**.

N-methyl-*N*-hexyl 1-[2-(diphenylphosphino)ferrocenyl]ethylamine, **2g**, a ligand whose structure is closely related to those of **2c**–**e** but lacks a triethoxysilyl group, was prepared from **2b** both via N-alkylation by 1-iodohexane and N-acylation by hexanoic acid in the presence of DCC[10] followed by LAH reduction. In addition, unsaturated analogs of **2g** bearing hexenyl- and hexynyl-

obtained in this way seemed to be relatively clean, simple passing of a solution of a crude complex in acetonitrile through a reversed-phase silica gel column would usually allow for a separation from at least two other colored bands. *P,P*-complex **3d** had to be grafted directly after preparation as passing its solution in acetonitrile through the column resulted in a partial oxidation of the ligand. Among the allyl signals only those of central CH were observed in the ^1H NMR spectra of the allyl palladium complexes taken in $CDCl_3$ at room temperature. In the ^1H NMR spectra of $[(\eta^3\text{-}C_3H_5)Pd(\mathbf{2c}–\mathbf{e})Cl]$ the *N*-methyl signals have clearly shifted downfield compared to those of the free ligands indicating that nitrogen is involved in coordination. Only one signal could be observed in the ^{31}P NMR spectra of the *P,N*-complexes in $CDCl_3$, while that of $[(\eta^3\text{-}C_3H_5)Pd(\mathbf{3d})Cl]$ displayed a broad signal and a doublet. However, in CD_3OD the spectrum of $[(\eta^3\text{-}C_3H_5)Pd(\mathbf{3d})Cl]$ appeared as an overlap between an AB quartet and a singlet. The ^1H NMR spectrum of the *P,P*-complex in CD_3OD suggested the presence of two isomers with different allyl orientation in 3:1 ratio. It was strikingly different from the spectrum

in $CDCl_3$ displaying an averaged picture due to a fast (on the NMR time-scale) interconversion of isomers. The plausible structures of these isomers are depicted in Fig. 2.

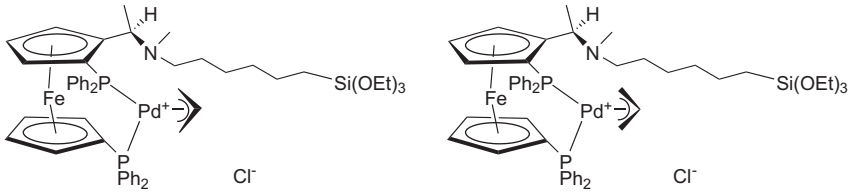


Fig. 2. Plausible isomeric structures of bisphosphine complex [(η^3-C_3H_5)Pd(**3d**)Cl].

Grafting of *P,N*-complexes or ligand (*S,R*)-**2d** was carried out by stirring 0.2 mmol of a compound with 1.0 g of mesoporous silica in toluene at 50 °C. Toluene–dichloromethane mixture (7:1) was used in case of [(η^3-C_3H_5)Pd(**3d**)Cl]. In all cases colorless solutions were obtained after the filtration of solids. Upon washing and drying in vacuo the solids were characterized by ^{31}P MAS-NMR. The phosphine signals of the complexes grafted onto mesoporous silica appeared around 15 ppm, which was in good agreement with those of homogeneous complexes (*S,R*)-**9**, (*R,S*)-**10**, and (*R,S*)-**11** obtained by ^{31}P NMR in solution. On the other hand, in spite of the same grafting conditions, the ^{31}P MAS-NMR of the ligand grafted onto mesoporous silica showed the existence of both oxidized and free forms of phosphine at 43.0 and −25.4 ppm, respectively. This result indicates that oxidation of a phosphine could happen upon grafting. For every supported catalyst its Pd content was measured by both ICP-AES and elemental analysis. In all cases the Pd contents were found to be 0.16 mmol/g according to both methods. For the sake of brevity the supported catalysts are designated according to their ligands' tethers, i.e., (*R,S*)-**COCPPF** corresponds to [(η^3-C_3H_5)Pd(*R,S*-**2e**)Cl] supported on mesoporous silica (Fig. 3).

2.3. Asymmetric allylic alkylation

Performance of the silica-supported catalysts was evaluated in a benchmark allylic substitution reaction between *rac*-1-acetoxy-1,3-diphenylprop-2-ene, **7**, and dimethyl malonate in the presence of *N,O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of potassium acetate. First, the dependence of activity (conversion of **7**) and enantioselectivity on tether for the supported catalysts derived from **2b** were evaluated in CH_2Cl_2 as a solvent (Table 2). For comparison, the data for homogeneous catalysts [(η^3-C_3H_5)Pd(*S,R*-**2g**)Cl] ((*S,R*)-**9**), [(η^3-C_3H_5)Pd(*R,S*-**2f**)Cl] ((*R,S*)-**10**), and [(η^3-C_3H_5)Pd(*R,S*-**2h**)Cl] ((*R,S*)-**11**) prepared in situ are also included, as the structures of these complexes are sufficiently close to those of the supported complexes (entries 4, 5, and 6). The catalyst obtained in situ by mixing ligand (*R,S*)-**2d** grafted onto mesoporous silica with [(η^3-C_3H_5)PdCl]$_2$ (grafting–ligation process) was also tested (entry 7). In addition, the data for the bisphosphine ligand catalyst with the C6 tether ((*R,S*)-**BPPF**, entry 8) is shown to illustrate the difference

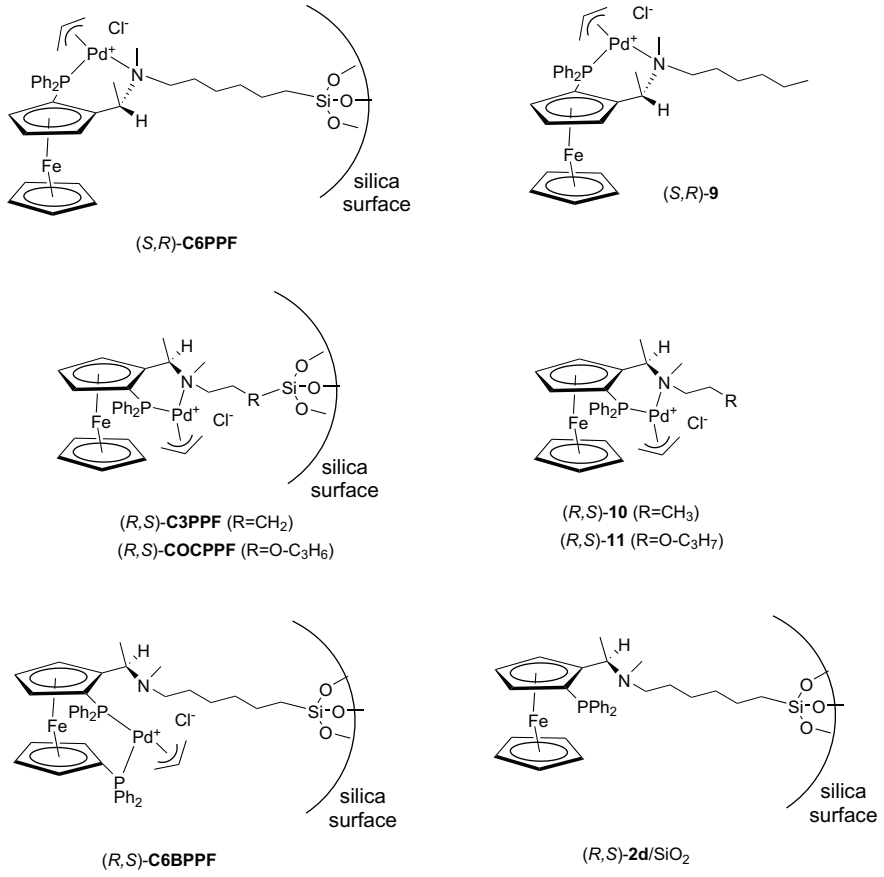
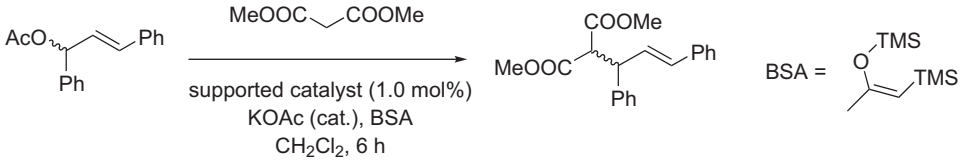


Fig. 3. Plausible structures of complexes and a ligand used as catalysts or a part of the catalyst in Table 2.

Table 2
Allylic alkylation of **7** with dimethyl malonate catalyzed by silica-suported and homogeneous catalysts in CH_2Cl_2



Entry	Catalyst name	Ligand	*N*-Alkyl chain of the ligand	Conversion[a] (Yield[b], %)	ee, %
1	(*S*,*R*)-**C6PPF**	(*S*,*R*)-**2d**	$(CH_2)_6Si$	100 (87)	50 (*R*)
2	(*R*,*S*)-**C3PPF**	(*R*,*S*)-**2c**	$(CH_2)_3Si$	100	23 (*S*)
3	(*R*,*S*)-**COCPPF**	(*R*,*S*)-**2e**	$(CH_2)_2O(CH_2)_3Si$	100	42 (*S*)
4	(*S*,*R*)-**9**	(*S*,*R*)-**2g**	$(CH_2)_6H$	100	59 (*R*)
5	(*R*,*S*)-**10**	(*R*,*S*)-**2f**	$(CH_2)_3H$	100	34 (*S*)
6	(*R*,*S*)-**11**	(*R*,*S*)-**2h**	$(CH_2)_2O(CH_2)_3H$	100	52 (*S*)
7	(*R*,*S*)-**2d**/SiO_2+$[(\eta^3\text{-}C_3H_5)PdCl]_2$[c]	(*R*,*S*)-**2d**	$(CH_2)_6Si$	30	27(*S*)
8	(*R*,*S*)-**C6BPPF**	(*R*,*S*)-**3d**	$(CH_2)_6Si$	100[d]	49 (*S*)

[a] Calculated from the ^1H NMR spectra of crude products.
[b] Isolated yield.
[c] $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (1:2 M ratio) was used.
[d] Reaction time 26 h.

between the monophosphine and bisphosphine catalysts. For every catalyst in Table 2 (except those in entries 7 and 8) the reaction was complete in less than 6 h furnishing expected product **8** in almost quantitative yield as a mixture of *R*- and *S*-enantiomers. The ees obtained with the supported catalysts were lower and followed a trend observed previously by Toma and co-workers[3a] for the **2b**-derived supported catalysts, that is, the longer the tether, the higher the enantioselectivity. For the catalyst obtained according to the generally used grafting—ligation procedure, i.e., formation of a chiral supported catalyst by combination of (*R*,*S*)-**2d**/SiO_2 with 0.5 equiv of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ in situ, both catalytic activity and enantioselectivity were lower than those for homogeneous catalyst (*S*,*R*)-**9** and heterogeneous catalyst (*S*,*R*)-**C6PPF** (entries 1, 4, and 7). The low catalytic activity could be explained by partial oxidation of the phosphine group of ligand (*R*,*S*)-**2d** on grafting.

For catalysts with tethers of the same length (entries 1, 3, 4, and 6) the presence of oxygen seems to be slightly disfavoring the enantioselectivity. For the *P*,*N*- and *P*,*P*-catalysts with C6 tethers (entries 1 and 8) there was a big difference in reaction rates, but almost no difference in enantioselectivity. Since (*S*,*R*)-**C6PPF** had emerged as the best catalyst in the monophosphine series, its performance in different solvents was examined next (Table 3).

Table 3
Allylic alkylation of **7** with dimethyl malonate catalyzed by (*S*,*R*)-**C6PPF** in different solvents

Entry	Solvent	Reaction Time, h	Conversion[a] (Yield[b], %)	ee, %
1	Toluene	22	100	40 (*R*)
2	THF	23	100	40 (*R*)
3	CH_2Cl_2	6	100 (87)	49 (*R*)
4[c]	CH_2Cl_2	6	22	47 (*R*)
5	Acetonitrile	1.5	100 (94)	53 (*R*)

[a] Calculated from the ^1H NMR spectra of crude products.
[b] Isolated yield.
[c] Reaction at 0 °C.

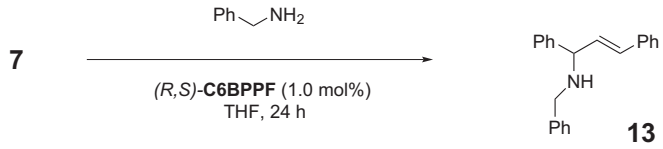
The data in Table 3 suggest that more polar solvents increase both the reaction rate and the enantioselectivity. Among the solvents evaluated the reaction in acetonitrile not only gave the highest ee, but was also the fastest. By way of comparison, reaction with homogeneous catalyst (*S*,*R*)-**9** in acetonitrile was completed in less than 1.5 h furnishing **8** in 63% ee. Lowering the reaction temperature from ambient to 0 °C brought about a significant decrease of the reaction rate without much effect on the enantioselectivity (entries 3 and 4).

To check whether there was any erosion of enantioselectivity reactions catalyzed by (*S*,*R*)-**C6PPF** in dichloromethane were stopped short of completion at 3 h and 30 min followed by product analysis. In the former case the enantioselectivity was 50% at 57% conversion, while in the latter case the result was inconclusive (enantioselectivity 56% at 11% conversion, but this was likely due to the overlap of (*R*)-**8** signal with those of a trace product, 1,3-diphenylprop-2-en-1-ol, in the chiral HPLC chromatogram).

Catalyst (*S*,*R*)-**C6PPF** already used once was inactive in the second run. The reasons for this behavior are unclear. One of the possibilities is that under the reaction conditions the metal complex supported on the surface of silica could leach in solution. Another possibility is decomposition of the supported catalyst leading to the formation of catalytically inactive species. This is indirectly corroborated by a gradual darkening of the reaction mixtures toward the completion of reactions. A combination of leaching and decomposition is also possible. The following two experiments were designed to probe if Si—O—Si bonds keeping the complex attached to the surface of silica can be broken under the reaction conditions. In the first one, two reaction tubes were set up. In tube A, a catalytic amount of (*S*,*R*)-**C6PPF** was stirred in dichloromethane with BSA and a catalytic amount of KOAc at room temperature for 3 h. The supernatant was carefully withdrawn with a syringe after centrifugation and added to tube B containing only substrate **7** and excess dimethyl malonate. Should any active complex leach into the solution in tube A, it would catalyze the reaction in tube B upon transfer. The analysis of the content of tube B after stirring for 6 h at room temperature followed by usual work-up showed 54% conversion of **7**. Thus, it appears that *in the absence of dimethyl malonate* in tube A the supported catalyst was leaching into the solution. However, in the second experiment where dimethyl malonate was placed in tube A instead of tube B, other things being the same, less than 5% conversion of **7** was detected in tube B. Thus, in the presence of dimethyl malonate leaching of an active catalytic species in solution appeared to be minimal. However, these results obtained in the absence of substrate **7** in tube A do not entirely exclude the possibility of leaching in the catalytic reaction, and additional experiments would be required to address this issue.

2.4. Asymmetric allylic amination

Supported catalyst (*S*,*R*)-**C6PPF**, which was very active in the allylic alkylation of **7** with dimethyl malonate in the presence of BSA, turned out to be completely ineffective for the allylic amination of **7** with benzyl amine in CH_2Cl_2. However, reaction with (*R*,*S*)-**C6BPPF** as a catalyst in THF resulted in complete conversion of **7** after 24 h of stirring at ambient temperature (Scheme 2).



Scheme 2.

Product **13** was isolated in 78% yield, its ee (38%) being significantly lower compared to that of (*S*)-**8** obtained with the same catalyst in CH_2Cl_2 (Table 2, entry 8). By comparison of the product chiral HPLC profiles to those reported in literature for the same chiral column the stereochemistry of the major enantiomer of **13** was assigned to (*R*).[11] Thus, the stereochemical outcomes of the allylic amination and alkylation reactions catalyzed by (*R*,*S*)-**C6BPPF** are the same (despite their products chiral descriptors being different). For a similar allylic amination of *rac*-1,3-diphenyl-2-propenyl carbonate using homogeneous catalysts prepared in situ from $Pd_2(dba)_3$–$CHCl_3$ and (*R*,*S*)-*N*-methyl-*N*-bis (hydroxymethyl)methyl or (*R*,*S*)-*N*,*N*-dimethyl 1-[1′,2-bis (diphenyl-phosphino)ferrocenyl]ethylamine ligands, formation of (*R*)-**13** with 97 and 31% ee, respectively, was reported by Hayashi and co-workers.[12] Interestingly, just like in the case of allylic alkylation using *P*,*N*-ligand complexes, changing the reaction solvent to more polar CH_2Cl_2 and acetonitrile resulted in moderate increases in enantioselectivity (46 and 52%, respectively). However, unlike the allylic alkylation case, this came at the expense of conversion as in neither solvent the reaction was complete after 24 h of stirring at room temperature. In addition, in the allylic amination of cinnamyl acetate with benzyl amine the *P*,*P*-supported catalyst was found to be more active than the *P*,*N*-catalyst with the same tether, although both failed to furnish any branched product, unlike Thomas' bisphosphine Pd catalyst **12** with the same number of atoms in the tether confined within the pores of MCM-41.[4a]

3. Conclusion

In this paper a general method of synthesis and purification of Ugi amine-derived *P*,*N*- and *P*,*P*-ligands with built-in triethoxysilyl groups attached via simple hydrocarbon chains has been presented. The approach used here can be potentially useful for the synthesis of other phosphine ligands provided they possess nitrogen or another heteroatom subject to alkylation in their structure. Unlike the usual approach of grafting ligands on silica followed by complexation with palladium, in this work the allyl palladium complexes with the *P*,*N*- and *P*,*P*-ligands were prepared first followed by their grafting on silica. In most cases this allowed for their proper purification and characterization prior to the reaction with support. The enantioselectivities demonstrated by the supported catalysts in both allylic alkylation and amination reactions, which can be described as moderate at best, are dependent on the solvent polarity, with acetonitrile being the best among the solvents studied. Although they are lower than the ones obtained with the model homogeneous catalysts, the drop in ee is not dramatic considering that the chosen model homogeneous catalysts themselves are capable of inducing only moderate ee's in these reactions. In the allylic alkylation reaction the increase of the *P*,*N*-ligand's tether length from C3 to C6 has resulted in the increase in ee, in accordance with the previous study on *P*,*P*-ligands.[3a] Unlike the *P*,*N*-complex with C6 tether, the corresponding *P*,*P*-complex was found to catalyze both the allylic alkylation and amination reactions.

4. Experimental section

4.1. General remarks

All reactions were run under nitrogen. All reaction solvents were dried according to the standard procedures unless stated otherwise. Column chromatography was performed on Wakogel C-300 silica gel (normal phase) or Wakogel 50C18 (reversed phase). Mesoporous silica (NPM 2.7, lot. No.71090, 2.7 nm averaged pore diameter) was obtained from Taiyo Kagaku Corporation. ^1H, ^{13}C, and ^{31}P NMR spectra in solution were recorded on a Bruker Avance 400 spectrometer operating at 400.1, 100.6, and 162.0 MHz, respectively. All ^1H and ^{13}C NMR spectra were referenced internally using residual chloroform signals in $CDCl_3$ (7.26 and 77.2 ppm, respectively). ^{31}P chemical shifts are reported externally relative to 85% aqueous H_3PO_4 (0.0 ppm). Solid-state ^{31}P MAS-NMR spectra were recorded on a Bruker Avance 400M spectrometer at 14.5 kHz scanning at room temperature. The ESIMS spectrum was obtained on a ThermoQuest Finnigan AQA system. Elemental analyses were performed on a CE Instruments EA1100. Inductively coupled plasma (ICP) analyses were carried out using Shimadzu ICPS-8100 system. Amine–phosphines **2b** and **3b** were prepared according to the method of Boaz and co-workers[13] *rac*-**7** was prepared according to the method of Auburn and co-workers.[14]

4.2. Synthesis of α,ω-iodo(triethoxysilyl)alkanes

4.2.1. 1-Iodo-6-(triethoxysilyl)hexane, ***5***. To a solution of 1-methanesulfonyloxy-hex-5-ene (2.6642 g, 14.946 mmol) in 20 mL THF was added the Karstedt's catalyst solution in xylene (18 drops) followed by dropwise addition of triethoxysilane (3.10 mL, 16.98 mmol) within 10 min. The reaction flask was placed in oil bath at 45 °C. To achieve complete conversion additional catalyst (4 drops) was syringed in 19 h later. After additional 22 h the reaction mixture was removed from the oil bath and stripped off the volatiles in vacuo. The leftover brown oil was mostly 1-methanesulfonyloxy-6-(triethoxysilyl)hexane according to its ^1H NMR ($CDCl_3$, 400.13 MHz): 4.21 (t, 2H, J=6.6, $MsOCH_2$), 3.81 (quartet, 6H, J=7.0, $SiOCH_2CH_3$), 2.99 (s, 3H, CH_3SO_3), 1.78–1.69 (m, 2H, $OCH_2CH_2CH_2$), 1.47–1.29 (m, 6H, $(CH_2)_3CH_2Si$), 1.22 (t, 9H, J=7.0, $SiOCH_2CH_3$), 0.65–0.59 (m, 2H, CH_2Si). Following the addition of NaI (4.4302 g, 29.556 mmol) and DMF (25 mL) into the same reaction flask the hydrosilylation product was heated to 55 °C for 4.5 h in the dark. After cooling, filtration and removal of most DMF in vacuo the resulting oil was stirred with hexane. Additional filtration, removal of volatiles, and crude product purification by Kugelrohr's distillation afforded the title compound in 34% yield. ^1H NMR ($CDCl_3$, 400.13 MHz): 3.81 (quartet, 6H, J=7.0, $SiOCH_2CH_3$), 3.18 (t, 2H, J=7.0, CH_2I), 1.81 (quintet, 2H, J=7.0, CH_2CH_2I), 1.47–1.29 (m, 6H, $CH_2CH_2CH_2CH_2Si$), 1.22 (t, 9H, J=7.0, $SiOCH_2CH_3$), 0.66–0.59 (m, 2H, CH_2Si). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): 58.51, 33.61, 32.15, 30.31, 22.79, 18.49, 10.50, 7.49. Anal. Calcd for $C_{12}H_{27}O_3SiI$: C, 38.50; H, 7.27. Found: C, 38.81; H, 7.25.

4.2.2. 1-Iodo-6-(triethoxysilyl)-3-oxahexane, ***6***. To a solution of 1-methanesulfonyl-oxy-3-oxa-hex-5-ene (1.3656 g, 7.577 mmol) in

THF (10 mL) was added the solution of Karstedt's catalyst in xylene (9 drops) followed by dropwise addition of triethoxysilane (1.60 mL, 8.77 mmol) within 10 min. The reaction flask was placed for 5 h into an oil bath pre-heated to 45 °C followed by removal of volatiles in vacuo. According to its ^{1}H NMR, the leftover brown oil was mostly 1-methanesulfonyl-oxy-6-(triethoxysilyl)-3-oxahexane (($CDCl_3$, 400.13 MHz): 4.37–4.34 (m, 2H, MsOCH_2), 3.81 (quartet, 6H, J=7.0, SiOCH_2CH$_3$), 3.70–3.67 (m, 2H, OCH_2CH$_2$OMs), 3.46 (t, 2H, J=6.6, OCH_2CH$_2$CH$_2$), 3.05 (s, 3H, CH_3SO$_3$), 1.73–1.65 (m, 2H, OCH$_2$CH_2CH$_2$), 1.22 (t, 9H, J=7.0, SiOCH$_2$CH_3), 0.65–0.60 (m, 2H, CH_2Si)). In the same reaction flask NaI (2.2740 g, 15.171 mmol) and DMF (16 mL) were added, and the resulting mixture was heated to 55 °C for 4.5 h in the dark. Residual oil left after cooling, filtration and removal of most of DMF in vacuo was stirred with hexane. Filtration, removal of volatiles in vacuo, and chromatography on a normal phase silica gel column (EtOAc/hexane, 1:2) furnished 1.5160 g (53% yield) of title compound as colorless oil. ^{1}H NMR ($CDCl_3$, 400.13 MHz): 3.82 (quartet, 6H, J=6.9, SiOCH_2CH$_3$), 3.68 (t, 2H, J=7.0, OCH_2CH$_2$I), 3.46 (t, 2H, J=6.6, OCH_2CH$_2$CH$_2$), 3.24 (t, 2H, J=6.8, CH_2I), 1.74–1.65 (m, 2H, OCH$_2$CH_2CH$_2$Si), 1.22 (t, 9H, J=7.0, SiOCH$_2$CH_3), 0.68–0.63 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.62 MHz): 73.19, 71.43, 58.53, 23.15, 18.46, 6.64, 3.38. Anal. Calcd for $C_{11}H_{25}O_4SiI$: C, 35.11; H, 6.70. Found: C, 34.43; H, 6.47.

4.2.3. General procedure for the alkylation of ***2b****.* A 50 mL two-neck round-bottomed flask equipped with a magnetic stirbar was charged in air with **2b** (0.4273 g, 1.000 mmol) and potassium carbonate (0.2073 g, 1.500 mmol). A short reflux condenser was attached to the central neck while the side neck was stoppered with a rubber septum. Under nitrogen a solution of iodoalkylsilane **4**–**6** (1.000 mmol) in 8 mL acetonitrile was syringed into the flask via the septum. The mixture was heated in an oil bath at 40 °C in the dark for 39–60 h depending on the iodoalkylsilane used. Volatiles were removed by pumping through a −196 °C trap followed by addition of CH_2Cl_2 (15 mL). After brief stirring the solution was filtered through a pad of Celite on a sintered glass frit into a 200 mL round-bottomed flask. The pad was washed with additional dichloromethane until it became colorless. The filtrate combined with the wash was stripped off the solvent on a rotary evaporator. The resulting dark oil was dissolved in 1 mL of acetonitrile and chromatographed on a reversed-phase silica gel column packed with 20–21 g of Wakogel 50C18 and acetonitrile. The desired tertiary amine was the last colored band eluted after those of the −onium salts and unreacted secondary amine. It was stripped off the solvent on a rotary evaporator and pumped on through a −196 °C trap overnight furnishing the desired tertiary amine−phosphine.

*4.2.4. N-Methyl-N-(3′-(1′-(triethoxysilyl)propyl))-1-[2-(diphenylphosphino)ferrocenyl]-ethylamine (****2c****).* Dark-orange oil, 57% yield. ^{1}H NMR ($CDCl_3$): 7.61–7.53 (m, 2H, C$_6H_5$), 7.38–7.33 (m, 3H, C$_6H_5$), 7.19–7.08 (m, 5H, C$_6H_5$), 4.38 (s, 1H, C$_5H_3$), 4.29–4.19 (m, 2H, C$_5H_3$, and CHCH$_3$), 3.91 (s, 5H, C$_5H_5$), 3.84 (s, 1H, C$_5H_3$), 3.73 (quartet, J=6.9, 6H, SiOCH_2CH$_3$), 2.37–2.27 (m, 1H, NCH_a), 2.21–2.11 (m, 1H, NCH_b), 1.67 (s, 3H, NCH_3), 1.26 (d, J=6.8, 3H, CHCH_3), 1.19 (t, J=6.9, 9H, SiOCH$_2$CH_3), 1.10–0.98 (m, 2H, CH$_2$CH_2CH$_2$), 0.39–0.28 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.33 (d, J=8.1), 139.28 (d, J=8.8), 135.57 (d, J=21.9), 132.41 (d, J=17.5), 128.88, 127.98 (d, J=8.0), 127.40 (d, J=5.8), 127.10, 97.45 (d, J=23.4), 76.40 (d, J=9.6), 71.92 (d, J=5.1), 69.80 (shoulder), 69.72, 68.52, 58.35, 58.17, 57.52 (d, J=6.5), 34.13, 20.83, 18.47, 9.66 (br), 7.99. ^{31}P{^{1}H} NMR ($CDCl_3$): −22.7. Anal. Calcd for $C_{34}H_{46}NO_3SiPFe$: C, 64.65; H, 7.34; N, 2.22. Found: C, 64.63; H, 7.29; N, 2.19.

*4.2.5. N-Methyl-N-(6′-(1′-(triethoxysilyl)hexyl))-1-[2-(diphenylphosphino)ferrocenyl]-ethylamine (****2d****).* Dark-orange oil, 65% yield. ^{1}H NMR ($CDCl_3$): 7.61–7.54 (m, 2H, C$_6H_5$), 7.38–7.32 (m, 3H, C$_6H_5$), 7.19–7.10 (m, 5H, C$_6H_5$), 4.39 (s, 1H, C$_5H_3$), 4.28–4.20 (m, 2H, C$_5H_3$, and CHCH$_3$), 3.92 (s, 5H, C$_5H_5$), 3.86–3.78 (overlapping quartet and singlet, J=6.9, 7H, SiOCH_2CH$_3$, and C$_5H_3$), 2.31–2.21 (m, 1H, NCH_a), 2.16–2.06 (m, 1H, NCH_b), 1.69 (s, 3H, NCH_3), 1.33–1.24 (overlapping multiplets, 5H, NCH$_2$CH_2CH$_2$, and CHCH_3), 1.23 (t, J=6.9, 9H, SiOCH$_2$CH_3), 1.17–1.07 (m, 2H, NCH$_2$CH$_2$CH_2), 0.99–0.74 (m, 4H, CH$_2$CH_2CH_2CH$_2$Si), 0.61–0.54 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.20 (d, J=8.1), 139.16 (d, J=8.1), 135.52 (d, J=21.2), 132.48 (d, J=18.3), 128.83, 127.96 (d, J=7.4), 127.41 (d, J=6.5), 127.18, 97.41 (poorly observed d), 76.37 (d, J=9.5), 71.94 (d, J=5.1), 69.82 (shoulder), 69.72, 68.45, 58.40, 57.58 (d, J=7.3), 54.51, 34.24, 33.40, 27.62, 27.25, 22.81, 18.47, 10.55, 9.42 (br). ^{31}P{^{1}H} NMR ($CDCl_3$): −22.8. Anal. Calcd for $C_{37}H_{52}NO_3SiPFe$: C, 65.96; H, 7.78; N, 2.08. Found: C, 65.84; H, 7.78; N, 2.07.

*4.2.6. N-Methyl-N-(6′-(1′-(triethoxysilyl)-4′-oxahexyl))-1-[2-(diphenylphosphino)ferro-cenyl]ethylamine (****2e****).* Dark-orange oil, 46% yield. ^{1}H NMR ($CDCl_3$): 7. 59–7.52 (m, 2H, C$_6H_5$), 7.37–7.32 (m, 3H, C$_6H_5$), 7.20–7.11 (m, 5H, C$_6H_5$), 4.38 (s, 1H, C$_5H_3$), 4.28–4.20 (m, 2H, C$_5H_3$, and CHCH$_3$), 3.93 (s, 5H, C$_5H_5$), 3.84–3.77 (overlapping quartet and singlet, 7H, J=7.0, 7H, SiOCH_2CH$_3$, and C$_5H_3$), 3.18–3.06 (m, 2H, OCH_2CH$_2$CH$_2$), 2.95–2.85 (m, 1H, NCH$_2$CH_aO), 2.70–2.60 (m, 1H, NCH$_2$CH_bO), 2.56–2.46 (m, 1H, NCH_a), 2.40–2.30 (m, 1H, NCH_b), 1.75 (s, 3H, NCH_3), 1.60–1.51 (m, 2H, OCH$_2$CH_2CH$_2$), 1.26 (d, J=6.8, 3H, CHCH_3), 1.22 (t, J=7.0, 9H, OCH$_2$CH_3), 0.59–0.53 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.14 (d, J=7.4), 138.87 (d, J=9.5), 135.44 (d, J=21.2), 132.51 (d, J=18.3), 128.84, 127.98 (d, J=8.0), 127.48 (d, J=5.9), 127.27, 97.29 (d, J=24), 76.33 (d, J=8.8), 73.26, 72.02 (d, J=5.1), 69.81 (shoulder), 69.72, 69.45, 68.43, 58.45, 57.99 (d, J=8.0), 53.10, 35.43, 23.06, 18.44, 9.34 (br), 6.62. ^{31}P{^{1}H} NMR ($CDCl_3$): −22.9. Anal. Calcd for $C_{36}H_{50}NO_4SiPFe$: C, 63.99; H, 7.46; N, 2.07. Found: C, 64.09; H, 7.40; N, 2.04.

*4.2.7. N-Methyl-N-(n-hexyl)-1-[2-(diphenylphosphino)ferrocenyl] ethylamine (****2g****).* Orange solid, 65% yield. ^{1}H NMR ($CDCl_3$): 7.61–7.54 (m, 2H, C$_6H_5$), 7.38–7.33 (m, 3H, C$_6H_5$), 7.19–7.10 (m, 5H, C$_6H_5$), 4.39 (s, 1H, C$_5H_3$), 4.28–4.20 (m, 2H, C$_5H_3$, and CHCH$_3$), 3.92 (s, 5H, C$_5H_5$), 3.85 (s, 1H, C$_5H_3$), 2.31–2.21 (m, 1H, NCH_a), 2.17–2.06 (m, 1H, NCH_b), 1.70 (s, 3H, NCH_3), 1.27 (d, 3H, CHCH_3), 1.20–1.01 (m, 4H, NCH$_2$CH_2CH_2), 0.94 (quintet, J=7.3, 2H, CH_2CH$_2$CH$_3$), 0.87–0.76 (m, 5H, CH$_2$CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.25 (d, J=8.9), 139.21 (d, J=9.6), 135.55 (d, J=21.2), 132.48 (d, J=18.2), 128.84, 127.97 (d, J=7.2), 127.40 (d, J=6.6), 127.15, 97.46 (d, J=23), 76.37 (d, J=8.8), 71.95 (d, J=5.8), 69.80 (shoulder), 69.73, 68.47, 57.59 (d, J=7.2), 54.55, 34.23, 32.00, 27.70, 27.27, 22.68, 14.28, 9.53 (br). ^{31}P{^{1}H} NMR ($CDCl_3$): −22.8. Anal. Calcd for $C_{34}H_{46}NO_3SiPFe$: C, 72.80; H, 7.49; N, 2.74. Found: C, 72.78; H, 7.44; N, 2.73.

Compounds **2f** and **2h** were prepared according to the above general procedure.

4.2.8. General procedure for the alkylation of ***3b****.* A 50 mL two-neck round-bottomed flask equipped with a magnetic stirbar was charged in air with **3b** (0.3058 g, 0.500 mmol) and potassium carbonate (0.1042 g, 0.754 mmol). A short reflux condenser was attached to the central neck while the side neck was stoppered with a rubber septum. Under nitrogen dichloromethane (method A-no addition, method B-1.0 mL, method C-2.0 mL) was added into the flask via the septum followed by a solution of iodoalkylsilane **4**–**6** (0.500 mmol) in 4 mL acetonitrile. The mixture was heated in an oil bath at 40 °C in the dark for 40–90 h depending on the iodoalkylsilane. Volatiles were removed by pumping through a −196 °C trap followed by addition of CH_2Cl_2 (15 mL). After brief stirring the solution was filtered through a pad of Celite on a sintered glass frit into a 200 mL round-bottomed flask. The pad was washed with additional dichloromethane until it became colorless. To the filtrate and wash combined Wakogel 50C18 silica gel (1.5 g) was added,

and the solvents were removed on the rotary evaporator. The resulting orange powder was placed atop column prepared from 14 to 15 g of Wakogel 50C18 silica gel and acetonitrile. The desired tertiary amine was the last colored band eluted after those of the salts and unreacted secondary amine. It was stripped off the solvent on the rotary evaporator and pumped on through −196 °C trap overnight furnishing the desired tertiary amine–bisphosphine.

*4.2.9. N-Methyl-N-(3″-(1″-(triethoxysilyl)propyl))-1-[1′,2-bis(diphenylphosphino)ferro-cenyl]ethylamine (**3c**).* Prepared in 33% (method A) or 45% yield (method B). ^{1}H NMR ($CDCl_3$): 7.52–7.46 (m, 2H, C_6H_5), 7.32–7.21 (m, 13H, C_6H_5), 7.18–7.05 (m, 5H, C_6H_5), 4.38 (br s, 1H, C_p), 4.36 (m, 1H, C_p), 4.23–4.14 (m, 1H, C*H*CH_3), 4.10–4.05 (m, 2H, C_p), 3.92 (br s, 1H, C_p), 3.74 (quartet, J=7.0, 6H, SiOC*H*$_2$$CH_3$), 3.66 (br s, 1H, C_p), 3.47 (m, 1H, C_p), 2.37–2.27 (m, 1H, NC*H*$_a$), 2.21–2.11 (m, 1H, NC*H*$_b$), 1.66 (s, 3H, NC*H*$_3$), 1.20 (t, J=7.0, 9H, OCH_2CH_3), 1.17 (d, 3H, J=6.4, $CHCH_3$), 0.39–0.32 (m, 2H, C*H*$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.3–127.0 (P(C_6H_5)$_2$), 98.29 (d, J=23.4, *C*PPh$_2$ of C_5H_3), 77.0–70.5 (C_5H_3 and C_5H_4), 58.34, 58.19, 57.30 (d, J=6.5), 34.01, 20.81, 18.47, 9.26 (br), 8.00. ^{31}P{^{1}H} NMR ($CDCl_3$): −17.0, −23.3. Anal. Calcd for $C_{46}H_{55}NO_3SiP_2Fe$: C, 67.72; H, 6.80; N, 1.72. Found: C, 68.01; H, 6.74; N, 1.65.

*4.2.10. N-Methyl-N-(6″-(1″-(triethoxysilyl)hexyl))-1-[1′,2-bis(diphenylphosphino)ferroce-nyl]ethylamine (**3d**).* Yield 48% (method C). ^{1}H NMR ($CDCl_3$): 7.51–7.45 (m, 2H, C_6H_5), 7.31–7.20 (m, 13H, C_6H_5), 7.16–7.04 (m, 5H, C_6H_5), 4.38–4.33 (m, 2H, C_p), 4.15 (qd, J=7.0, J=2.6, 1H, C*H*CH_3), 4.07 (septet, J=1.2, 1H, C_p), 4.05 (br t, 1H, C_p), 3.94–3.91 (m, 1H, C_p), 3.80 (quartet, J=7.0, 6H, SiOC*H*$_2$$CH_3$), 3.63 (br s, 1H, C_p), 3.48–3.46 (m, 1H, C_p), 2.27–2.18 (m, 1H, NC*H*$_a$), 2.11–2.03 (m, 1H, NC*H*$_b$), 1.64 (s, 3H, NC*H*$_3$), 1.31–0.70 (m, 8H, $NCH_2(CH_2)_4CH_2$), 1.22 (t, J=7.1, 9H, OCH_2CH_3), 1.14 (d, J=6.6, 3H, $CHCH_3$), 0.59–0.53 (m, 2H, C*H*$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.2–127.1 (P(C_6H_5)$_2$), 98.28 (d, J=22.7, *C*PPh$_2$ of C_5H_3), 77.0–70.5 (C_5H_3 and C_5H_4), 58.36, 57.32 (J=7.3), 54.43, 34.15, 33.35, 27.58, 27.24, 22.78, 18.45, 10.54, 9.05 (br). ^{31}P{^{1}H} NMR ($CDCl_3$): −16.8, −23.3. Anal. Calcd for $C_{49}H_{61}NO_3SiP_2Fe$: C, 68.60; H, 7.17; N, 1.63. Found: C, 69.11; H, 7.16; N, 1.60.

*4.2.11. N-Methyl-N-(6″-(1″-(triethoxysilyl)-4″-oxahexyl))-1-[1′,2-bis(diphenylphosphino)-ferrocenyl]ethylamine (**3e**).* Yield 24% (method A). ^{1}H NMR ($CDCl_3$): 7.50–7.44 (m, 2H, C_6H_5), 7.32–7.20 (m, 13H, C_6H_5), 7.19–7.06 (m, 5H, C_6H_5), 4.37–4.33 (m, 2H, C_p), 4.20–4.11 (m, 1H, C*H*CH_3), 4.07 (m, 1H, C_p), 4.04 (br s, 1H, C_p), 3.96 (br s, 1H, C_p), 3.81 (quartet, J=7.0, 6H, SiOC*H*$_2$$CH_3$), 3.62 (br s, 1H, C_p), 3.49 (m, 1H, C_p), 3.17–3.04 (m, 2H, $OCH_2CH_2CH_2$), 2.94–2.83 (m, 1H, NCH_2CH_aO), 2.68–2.58 (m, 1H, NCH_2CH_bO), 2.54–2.43 (m, 1H, NC*H*$_a$), 2.37–2.26 (m, 1H, NC*H*$_b$), 1.71 (s, 3H, NC*H*$_3$), 1.59–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.22 (t, J=7.0, 9H, OCH_2CH_3), 1.15 (d, 3H, J=6.8, $CHCH_3$), 0.58–0.52 (m, 2H, C*H*$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 141.1–127.2 (P(C_6H_5)$_2$), 97.85 (d, J=22.7, *C*PPh$_2$ of C_5H_3), 77.0–70.5 (C_5H_3 and C_5H_4), 73.29 (CH_2O), 69.48 (CH_2O), 58.49, 57.79 (d, J=7.0), 53.10, 35.39, 23.08, 18.47, 9.05 (br), 6.64. ^{31}P{^{1}H} NMR ($CDCl_3$): −17.0, −23.6. Anal. Calcd for $C_{48}H_{59}NO_4SiP_2Fe$: C, 67.05; H, 6.92; N, 1.63. Found: C, 66.79; H, 6.85; N, 1.57.

4.2.12. General procedure for the syntheses of P,N-allyl palladium complexes. A 2-neck 50 mL round-bottomed flask equipped with a magnetic stirbar was charged with a solution of a ligand (0.25–0.50 mmol) in CH_2Cl_2. The side neck was plugged with a septum, the central neck was attached to a vacuum line, and the solvent was removed by pumping on the stirred solution through a −196 °C trap. [(η^3-C_3H_5)PdCl]$_2$ was added via the side neck (2:1 ligand-dimer molar ratio). After evacuation and refill with nitrogen CH_2Cl_2 (5–10 mL) was added via a syringe followed by stirring for 1 h at ambient temperature and solvent removal in vacuo. The residue was dissolved in 1.0–1.5 mL of acetonitrile and placed atop a column packed with Wakogel 50C18 silica gel (12–16 g) using the same solvent. Upon elution with acetonitrile three colored bands were typically observed, the second one being that of the desired complex. While there was no clear-cut separation between the first (lightly-colored) and the second band (dark), the third one did not move at all. The complex was obtained by removal of acetonitrile in vacuo.

[(η^3-C_3H_5)*Pd*(**2c**)]*Cl*. Fluffy orange solid, 76% yield. ^{1}H NMR ($CDCl_3$): 8.29–8.21 (m, 2H, C_6H_5), 7.52–7.47 (m, 3H, C_6H_5), 7.28–7.24 (m, 3H, C_6H_5), 7.16–7.10 (m, 2H, C_6H_5), 5.53 (quintet, ^3J=10.0, 1H, C*H*$_{central}$), 5.13 (br s, 1H, C*H*CH_3), 4.50 (br s, 1H, C_5H_3), 4.38 (t, J=2.4, 1H, C_5H_3), 4.17 (br s, 1H, C_5H_3), 4.00 (s, 5H, C_5H_5), 3.71 (quartet, J=7.0, 6H, SiOC*H*$_2$$CH_3$), 2.41–2.33 (m, 4H, NC*H*$_3$, and NC*H*$_a$), 2.17 (br s, 1H, NC*H*$_b$), 1.38–1.22 (m, 5H, $CHCH_3$, and $NCH_2CH_2CH_2Si$), 1.15 (t, J=7.0, 9H, OCH_2CH_3), 0.40–0.34 (m, 2H, C*H*$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 139.2–127.6 (P(C_6H_5)$_2$), 118.49 (*C*H$_{central}$), 96.25 (d, J=15), 72.6–69.9 (C_5H_3 and C_5H_5), 58.41, 57.95, 55.84, 41.17, 21.98, 18.42, 10.50, 8.38. ^{31}P{^{1}H} NMR ($CDCl_3$): 11.1. Anal. Calcd for $C_{37}H_{51}NO_3SiPClFePd$: C, 54.56; H, 6.31; N, 1.72. Found: C, 54.43; H, 6.31; N, 1.66.

[(η^3-C_3H_5)*Pd*(**2d**)]*Cl*. Glassy dark-red solid, 85% yield. ^{1}H NMR ($CDCl_3$): 8.28–8.20 (m, 2H, C_6H_5), 7.52–7.46 (m, 3H, C_6H_5), 7.30–7.20 (m, 3H, C_6H_5), 7.14–7.06 (m, 2H, C_6H_5), 5.52 (quintet, ^3J=10.0, 1H, C*H*$_{central}$), 5.20 (br s, 1H, C*H*CH_3), 4.50 (br s, 1H, C_5H_3), 4.39 (t, J=2.4, 1H, C_5H_3), 4.17 (br s, 1H, C_5H_3), 3.98 (s, 5H, C_5H_5), 3.79 (quartet, J=7.0, 6H, SiOC*H*$_2$$CH_3$), 2.45 (s, 3H, NC*H*$_3$), 2.35 (td, J=11.6, 1H, NC*H*$_a$), 2.15–2.04 (br s, 1H, NC*H*$_b$), 1.35 (d, J=6.4, 3H, $CHCH_3$), 1.32–0.98 (m, 8H, $NCH_2(CH_2)_4CH_2Si$), 1.20 (t, J=7.0, 9H, OCH_2CH_3), 0.58–0.51 (m, 2H, C*H*$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 138.7–127.5 (P(C_6H_5)$_2$), 118.40 (*C*H$_{central}$), 95.94 (d, J=17.0), 72.6–69.9 (C_5H_3 and C_5H_5), 58.25, 58.16, 52.57, 42.18, 33.16, 28.68, 27.29, 22.73, 18.31, 10.35 (overlap of two signals). ^{31}P{^{1}H} NMR ($CDCl_3$): 11.6. MS (ESI): m/z 820.5 [M−Cl]$^+$. Anal. Calcd for $C_{40}H_{57}NO_3SiPClFePd$: C, 56.08; H, 6.71; N, 1.63. Found: C, 55.27; H, 6.47; N, 1.54.

[(η^3-C_3H_5)*Pd*(**2e**)]*Cl*. Glassy dark-red solid, 81% yield. ^{1}H NMR ($CDCl_3$): 8.26–8.18 (m, 2H, C_6H_5), 7.50–7.43 (m, 3H, C_6H_5), 7.28–7.20 (m, 3H, C_6H_5), 7.15–7.08 (m, 2H, C_6H_5), 5.55 (quintet, ^3J=10.0, 1H, C*H*$_{central}$), 5.00 (br s, 1H, C*H*CH_3), 4.49 (br s, 1H, C_5H_3), 4.36 (unresolved t, 1H, C_5H_3), 4.10 (br s, 1H, C_5H_3), 4.03 (s, 5H, C_5H_5), 3.78 (quartet, J=7.0, 6H, SiOC*H*$_2$$CH_3$), 3.25–3.11 (m, 4H, CH_2OCH_2), 2.69–2.60 (m, 1H, NC*H*$_a$), 2.52–2.41 (br s, 1H, NC*H*$_b$), 2.24 (s, 3H, NC*H*$_3$), 1.60–1.52 (m, 2H, $OCH_2CH_2CH_2$), 1.31 (d, J=6.4, 3H, $CHCH_3$), 1.19 (t, J=7.0, 9H, OCH_2CH_3), 0.57–0.51 (m, 2H, C*H*$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$): 139.63–127.54 (P(C_6H_5)$_2$), 118.42 (*C*H$_{central}$), 96.42 (d, J=17.6), 73.61 (CH_2OCH_2), 72.9–69.8 (C_5H_3 and C_5H_5), 70.39 (CH_2OCH_2), 58.51, 57.34, 51.70, 39.92, 23.14, 18.46, 10.21, 6.70. ^{31}P{^{1}H} NMR ($CDCl_3$): 10.3. Anal. Calcd for $C_{39}H_{55}NO_4$-SiPClFePd: C, 54.55; H, 6.46; N, 1.63. Found: C, 54.94; H, 6.32; N, 1.56.

[(η^3-C_3H_5)*Pd*(**2f**)]*Cl*. Fluffy orange solid, yield undetermined. ^{1}H NMR ($CDCl_3$): 8.20–8.10 (m, 2H, C_6H_5), 7.45–7.40 (m, 3H, C_6H_5), 7.22–7.12 (m, 3H, C_6H_5), 7.06–7.00 (m, 2H, C_6H_5), 5.47 (quintet, ^3J=10.0, 1H, C*H*$_{central}$), 5.11 (br s, 1H, C*H*CH_3), 4.44 (s, 1H, C_5H_3), 4.32 (s, 1H, C_5H_3), 4.11 (s, 1H, C_5H_3), 3.88 (s, 5H, C_5H_5), 2.40 (s, 3H, NC*H*$_3$), 2.24 (m, 1H, NC*H*$_a$), 2.03 (br s, 1H, NC*H*$_b$), 1.35 (d, ^3J=6.4, 3H, $CHCH_3$), 1.30–1.00 (m, 4H, $(CH_2)_2CH_3$), 0.60 (t, J=7.0, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): 134.66–126.53 (P(C_6H_5)$_2$), 117.39 (*C*H$_{central}$), 95.00 (weak signal), 71.32–68.90 (C_5H_3 and C_5H_5), 57.00, 53.53, 40.64, 20.82, 10.73, 0.83. ^{31}P{^{1}H} NMR ($CDCl_3$): 12.0.

[(η^3-C_3H_5)*Pd*(**2g**)]*Cl*. Fluffy orange solid, yield undetermined. ^{1}H NMR ($CDCl_3$): 8.25–8.16 (m, 2H, C_6H_5), 7.51–7.45 (m, 3H, C_6H_5), 7.30–7.19 (m, 3H, C_6H_5), 7.12–7.05 (m, 2H, C_6H_5), 5.54 (quintet, ^3J=10.0, 1H, C*H*$_{central}$), 5.22 (br s, 1H, C*H*CH_3), 4.50 (s, 1H, C_5H_3), 4.39 (s, 1H, C_5H_3), 4.18 (s, 1H, C_5H_3), 3.94 (s, 5H, C_5H_5), 2.52 (s, 3H, NC*H*$_3$), 2.35 (partially resolved td, 1H, NC*H*$_a$), 2.10 (br s, 1H, NC*H*$_b$), 1.35 (d,

^3J=6.4, 3H, CHCH_3), 1.31–0.93 (m, 8H, $CH_2(CH_2)_4CH_3$), 0.79 (t, ^3J=7.0, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 138.71–127.78 (P(C_6H_5)$_2$), 118.61 ($CH_{central}$), 96.05 (d, J=20.5), 72.7–70.0 (C_5H_3 and C_5H_5), 58.39, 52.71, 42.55, 31.99, 28.92, 27.43, 22.69, 14.13, 10.49. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 11.4.

[(η^3-C_3H_5)*Pd*(**2h**)]*Cl*. Glassy dark-red solid, yield undetermined. ^1H NMR ($CDCl_3$): 8.29–8.19 (m, 2H, C_6H_5), 7.53–7.49 (m, 3H, C_6H_5), 7.32–7.23 (m, 3H, C_6H_5), 7.19–7.09 (m, 2H, C_6H_5), 5.59 (br, 1H, $CH_{central}$), 5.03 (br s, 1H, $CHCH_3$), 4.53 (s, 1H, C_5H_3), 4.39 (s, 1H, C_5H_3), 4.12 (s, 1H, C_5H_3), 4.05 (s, 5H, C_5H_5), 3.28–3.10 (m, 4H, CH_2OCH_2), 2.75–2.62 (m, 1H, NCH_a), 2.52 (br s, 1H, NCH_b), 2.31 (s, 3H, NCH_3), 1.45 (m, 2H, $OCH_2CH_2CH_2$), 1.34 (br, 2H, $CHCH_3$), 0.84 (t, J=7.0, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 138.32–126.37 (P(C_6H_5)$_2$), 117.42 ($CH_{central}$), 95.64, 71.79–68.74 (C_5H_3 and C_5H_5), 56.32, 50.55, 38.92, 28.62, 21.76, 9.50. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 11.1.

[(η^3-C_3H_5)*Pd*(**3d**)]*Cl*. The crude complex was obtained by stirring a solution of **3d** (0.192 mmol) and [(η^3-C_3H_5)PdCl]$_2$ (0.098 mmol) in CH_2Cl_2 (4.0 mL) for 1 h. Upon addition of hexane (45 mL, freshly opened bottle) via a syringe a yellow precipitate has formed. The stirring was turned off to let it settle, and the supernatant was carefully withdrawn using a syringe. The precipitate was stirred with a fresh portion of hexane (15 mL) followed by the wash withdrawal and pumping on the residual solid via a −196 °C trap overnight furnishing a yellow solid (0.1284 g, 65% yield). ^1H NMR ($CDCl_3$): 7.80–7.10 (m, 20H, C_6H_5), 5.89 (very broad, $CH_{central}$), 4.62 (s, 1H, C_p), 4.56–3.56 (br m, C_p, and $CH_{terminal}$), 4.41 (t, J=2.4, 1H, C_p), 4.37 (s, 1H, C_p), 4.31 (s, 1H, C_p), 4.27 (s, 1H, C_p), 3.79 (q, J=7.1, 6H, OCH_2CH_3), 2.35 (partially resolved td, 1H, NCH_a), 2.07 (br s, 1H, NCH_b), 1.90 (s, 3H, NCH_3), 1.33–0.92 (m, $NCH_2(CH_2)_4CH_2$, and $CHCH_3$), 1.22 (t, J=7.1, 9H, OCH_2CH_3), 0.67 (br s, 1H), 0.59–0.54 (m, 2H, CH_2Si). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 136.2–127.6 (P(C_6H_5)$_2$), 120.97 ($CH_{central}$), 98.06, 78.3–70.6 (C_5H_3 and C_5H_4), 58.99, 58.44, 55.43, 34.12, 33.43, 28.04, 27.49, 22.84, 18.46, 10.55, 9.62. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 23.7 (d, J=37.6), 22.6 (br s). MS (ESI): m/z 1004.9 $[M-Cl]^+$. Anal. Calcd for $C_{52}H_{66}NO_3SiP_2ClFePd$: C, 60.00; H, 6.39; N, 1.35. Found: C, 59.77; H, 6.32; N, 1.31.

4.2.13. General procedure for the grafting of P,N-allyl palladium complexes and ligand ***2d***. A 200 mL 2-neck pea-shaped flask equipped with a magnetic stirbar was charged with 1.00 g of mesoporous silica. The side neck was plugged with a rubber septum, and the central neck was attached to a vacuum line via a glass adapter. After careful evacuation and refill with nitrogen toluene (10.0 mL) was added via a syringe. A solution of a complex (0.20 mmol) in toluene was added via a syringe. The flask was placed in an oil bath pre-heated to 50 °C and kept there for 7 h. After cooling under nitrogen overnight the solid was filtered off in air using a sintered glass frit and washed with toluene (5–10 mL). Both filtrate and wash were colorless. After drying in air for 3 h the solid was transferred into a pre-weighed 50 mL glass tube and pumped on for at least 24 h (−196 °C trap). The Pd and C, H, N contents in all supported materials were determined by ICP-AES and/or elemental analyses.

[(η^3-C_3H_5)*Pd*(**2c**)]*Cl*/*SiO*$_2$, (*R*,*S*)-**C3PPF**. Peach-colored solid, Pd content 1.7 wt %. $^{31}P\{^1H\}$ MAS-NMR (161.96 MHz): 16.7. Anal. Calcd found: C, 7.55; H, 1.21; N, 0.23.

[(η^3-C_3H_5)*Pd*(**2d**)]*Cl*/*SiO*$_2$, (*R*,*S*)-**C6PPF**. Peach-colored solid, Pd content 1.7 wt %. $^{31}P\{^1H\}$ MAS-NMR (161.96 MHz): 15.0. Anal. Calcd found: C, 8.05; H, 1.24; N, 0.24.

[(η^3-C_3H_5)*Pd*(**2e**)]*Cl*/*SiO*$_2$, (*R*,*S*)-**COCPPF**. Peach-colored solid, Pd content 1.7 wt %. $^{31}P\{^1H\}$ MAS-NMR (161.96 MHz): 16.8. Anal. Calcd found: C, 7.76; H, 1.29; N, 0.23.

2d/*SiO*$_2$, (*R*,*S*)-**C6**/SiO_2 light orange-colored solid, $^{31}P\{^1H\}$ MAS-NMR (161.96 MHz): 43.0 (phosphine oxide), −25.4 (phosphine). Anal. Calcd found: C, 9.50; H, 1.68; N, 0.21.

Grafting of [(η^3-C_3H_5)*Pd*(**3d**)]*Cl*. Due to its low solubility in toluene, first the *P*,*P*-complex (0.20 mmol) and mesoporous silica (1.00 g) were placed in the flask followed by evacuation, refill with nitrogen and addition of CH_2Cl_2 (6.5 mL) and toluene (43.5 mL). The rest of the procedure was identical to the general procedure for the grafting of a *P*,*N*-complex.

(*R*,*S*)-**C6BPPF**. Beige solid, Pd content 1.7 wt %. Anal. Calcd found: C, 9.51; H, 1.68; N, 0.21.

4.3. Asymmetric catalytic reactions

*4.3.1. Allylic alkylation of rac-***7** *with dimethyl malonate.* A 10 mL glass tube equipped with a magnetic stirbar was charged with 0.5 mmol of **7**, a supported catalyst (containing approximately 1 mol % Pd), and a pinch of KOAc. After sealing with a rubber septum the tube was evacuated via a stainless steel needle and refilled with nitrogen. Dry solvent (2 mL) was added followed by dimethyl malonate (0.5 mmol) and 1.5 mmol of *N*,*O*-bis(trimethylsilyl)acetamide. After stirring for an appropriate period of time the tube was centrifuged and opened. The supernatant was withdrawn with a pipet and diluted with EtOAc. The resulting solution was added to 25 mL of satd aq NH_4Cl and stirred briefly, then extracted with EtOAc (2×15 mL). The extract was dried over $MgSO_4$ and stripped off volatiles on a rotary evaporator. Conversion was calculated from a ^1H NMR spectrum of the crude product. Enantiomeric excess was determined using a Daicel Chiralpak IC column (eluent 80% hexane/20% *i*-PrOH/ethanolamine (199:1.0), flow rate 1.0 mL/min).

Allylic alkylation of *rac*-**7** using in situ generated catalyst was carried out as follows. A 10 mL glass tube equipped with a magnetic stirbar was charged with supported ligand (*R*,*S*)-**2d**/SiO_2 (approximately 1 mol %), a half molar equivalent of [(η^3-C_3H_5)PdCl]$_2$ and a pinch of KOAc. After sealing with a rubber septum the tube was evacuated via a stainless steel needle and refilled with nitrogen. Then dry CH_2Cl_2 (2 mL) was added followed by stirring for 1 h at room temperature. Dimethyl malonate (0.5 mmol) and 1.5 mmol of *N*,*O*-bis(trimethylsilyl)acetamide were added to the reaction mixture via a syringe. After stirring for 40 h the tube was centrifuged and opened. The reaction mixture was treated as described above.

*4.3.2. Allylic amination of rac-***7** *with benzyl amine.* A 10 mL glass tube equipped with a magnetic stirbar was charged with 0.5 mmol of **7** and a supported catalyst (containing approximately 1 mol % Pd). After sealing with a rubber septum the tube was evacuated via a stainless steel needle and refilled with nitrogen. Dry solvent (2 mL) was added followed by benzyl amine (1.5 mmol). After stirring for an appropriate period of time the tube was centrifuged and opened. The supernatant was withdrawn with a pipet and diluted with EtOAc (20 mL). The tube containing the supported catalyst was washed with 4 mL of EtOAc/hexane (1:1) and centrifuged again. The wash was combined with the crude product in EtOAc, and the resulting solution was added to 25 mL of satd aq NH_4Cl and stirred briefly, then extracted with EtOAc (2×15 mL). The extract was dried over Na_2SO_4, filtered, and stripped off volatiles on a rotary evaporator. Enantiomeric excess was determined using a Daicel Chiralpak IB column (eluent hexane/*i*-PrOH/DEA (100:0.5:0.1), flow rate 1.0 mL/min).

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Supplementary data

Experimental details of the synthetic approaches other than N-alkylation processes and the NMR spectra (^{1}H, ^{13}C, ^{31}P, and ^{31}P MAS) of new compounds are given. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.01.025.

References and notes

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